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Request for grant of a patent

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1. Your reference — PQ 12,835

2. Patent application number *(The Patent Office will fill in this part)* — 24 AUG 1999 — **9919906.9**

3. Full name, address and postcode of the or of each applicant *(underline all surnames)*

   CENTRAL RESEARCH LABORATORIES LIMITED
   DAWLEY ROAD
   MAYES
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   UB3 1HH

   Patents ADP number *(if you know it)*

   If the applicant is a corporate body, give the country/state of its incorporation — UK 609 794 3001

4. Title of the invention

   GAS SENSOR AND METHOD OF MANUFACTURE

5. Name of your agent *(if you have one)* — QED I.P. SERVICES LIMITED

   "Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*

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6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number

Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
—		

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing *(day / month / year)*
—	

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*

   a) any applicant named in part 3 is not an inventor, or
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   c) any named applicant is a corporate body.
   See note (d))

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Continuation sheets of this form	
Description	9
Claim*(s)*	4
Abstract	—
Drawing*(s)*	2

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Priority documents	—
Translations of priority documents	—
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	—
Request for preliminary examination and search *(Patents Form 9/77)*	1
Request for substantive examination *(Patents Form 10/77)*	—
Any other documents *(please specify)*	—

11. I/We request the grant of a patent on the basis of this application.

Signature [signature] Date 23 AUG 1999

12. Name and daytime telephone number of person to contact in the United Kingdom NEVILLE WALKER 0181 848 6692

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GAS SENSOR AND METHOD OF MANUFACTURE

The present invention relates to a gas sensor, and to a method of manufacturing the gas sensor. It relates particularly, but not exclusively, to a gas sensor for sensing carbon monoxide gas.

An electrochemical gas sensor for sensing an oxidisible or reducible gas such as carbon monoxide usually includes a sensing electrode, a counter electrode and a diffusion barrier. The diffusion barrier allows the gas which is to be sensed to pass to the sensing electrode. In one type of gas sensor as described, for example, in the Applicant's copending International Patent Application No. WO-A1-9614576, the sensing and counter electrodes are located on a gas permeable membrane and are in contact with an electrolyte.

During operation of the gas sensor, an electrochemical reaction occurs at the sensing electrode with the gas to be sensed, and a reaction also occurs with oxygen at the counter electrode. Electric current is carried through the electrolyte by ions produced in these reactions, and the amount of current indicates the concentration of the gas being sensed. A further electrode (the reference electrode) may be employed, for example, in combination with a potentiostat circuit, to maintain a constant potential difference between the sensing electrode and the electrolyte. This increases the stability of operation of the sensor.

In terms of physical construction, gas sensors usually comprise an external housing which acts as a reservoir for electrolyte, a wick to keep the electrolyte in contact with the electrodes, and external electrical terminals which make electrical contact with the electrodes. Such a gas sensor is described in the Applicant's published International Patent Application No. WO-A1-9614576.

External electrical terminals are usually formed from brass or copper pins. Brass and copper both react with the acid electrolyte, and so the gas sensor has to be

specially designed so that the pins do not come into contact with the electrolyte. Platinum does not react with acid, and so platinum strips can be also used to form an electrical path between the electrodes and an external electrical supply. However, platinum strips are commonly placed in the seal between the housing and the gas permeable membrane, and electrolyte can leak from this region. Platinum is also expensive, and so gas sensors having platinum terminals are expensive to manufacture.

An aim of the present invention is to provide a gas sensor that is cheaper to manufacture than existing gas sensors. Another aim of the invention is to provide a gas sensor that is less prone to leaking than existing gas sensors.

According to a first aspect of the invention there is provided a method of manufacturing a gas sensor comprising the steps of: 1) forming at least and first and second electrodes on a planar substrate; 2) forming external connection means on the substrate; 3) introducing conductive material into a portion of the substrate adjacent the external connection means, and into the portion of electrode adjacent said portion of substrate, so that an electrical path is formed between an electrode and the external connection means; 4) providing a housing containing a reservoir for liquid electrolyte; and 5) bonding the substrate and the housing so that a seal is formed which substantially prevents the leakage of electrolyte from the gas sensor.

Thus in accordance with the invention, a simple and reliable means is made of connecting one or more electrodes of the gas sensor to the external world, avoiding the use of expensive platinum terminals and producing a gas sensor which is less prone to leaking.

The method may also include the step of attaching a wicking means to the electrodes. The wicking means ensures that the electrodes are kept in contact with the electrolyte. The wicking means may be pressed or sintered to the electrodes at a temperature of between 300°C and 370°C, most preferably between 320°C and 370°C. The exact temperature depends on the nature of the wicking means, the

electrode material, and the substrate. This step may be performed before the melted polymer electrolyte is introduced, in which case the wicking means may have at least one aperture therein through which the polymer can pass to an electrode.

The conductive material may be introduced into the substrate via the wicking means, the electrodes, the external connection means, via the substrate, or via a combination of these methods.

The conductive material preferably includes polymer electrolyte, and is preferably introduced into the substrate in its melted state. On cooling and solidification of the conductive material, an electrical path is formed between the electrode and the external connection means. Alternatively, a plug, pin or other shaped component which contains a conductive polymer may be used, in which case the components may be inserted into apertures formed in the membrane, electrodes and/or external connection means, and swaged or melted into position. Current generated at the sensing electrode may thus pass via the substrate to the external connection means, and then to a suitable electronic device where the amount of current generated at the sensing electrode can be measured.

The first and second electrodes are preferably formed from a porous electrically conductive material containing PTFE or similar polymeric binder. The electrodes may also contain particles of catalyst, and optional additional catalyst support material and material to enhance conductivity.

The electrodes may be formed on the substrate by, for example, screen printing, filtering in selected areas from a suspension placed onto the substrate, by spray coating, sintering, or any other method suitable for producing a patterned deposition of solid material. Deposition might be of a single material, or of more than one material sequentially in layers so as, for example, to vary the properties of the electrode material through its thickness.

Preferably the first and second electrodes are formed on the opposite side of the substrate to the external electrical contact means. Alternatively, the first and second

electrodes and the external electrical contact means may be formed on the same side of the substrate.

The substrate may be bonded to the housing using adhesive. Alternatively, a mechanical means such as a snap-link may be used. It is preferred, however, to employ heat and/or pressure to bond the substrate to the housing. The housing is preferably composed of a synthetic plastics material with a lower melting point than the substrate. When the substrate and the housing are fixed together using heat and/or pressure, housing material impregnates the substrate thereby forming a strong bond.

A cap member having a diffusion barrier may also be provided. The substrate is then positioned between the cap member and the housing, and heat/and or pressure (or other suitable method) applied to seal the assembly. If a cap member is not used, then the permeability of at least one region of the substrate to gases may be controlled in order to limit the amount of gas reaching the sensing electrode. This may be achieved by use of a material with the required porosity, or the porosity may be decreased by i) compressing the region, ii) by impregnating the region(s) with, for example, wax, polymer, or a wax/polymer mix.

According to a second aspect of the invention there is provided a gas sensor comprising: 1) at least first and second electrodes formed on a planar substrate; 2) a housing containing a reservoir which, in use, contains liquid electrolyte for contacting the first and second electrodes; 3) external connection means, in contact with the substrate, for making external electrical connection to the gas sensor; and 4) a conductive mass disposed between an electrode and the external connection means, wherein at least a portion of the electrode and the portion of substrate substantially adjacent thereto is impregnated by the conductive mass, the conductive mass forming an electrical path between the electrodes and the external connection means.

The electrodes are preferably porous planar elements. The first electrode is preferably a gas sensing or working electrode for creating the desired

electrochemical reaction between the electrolyte and the gas to be sensed. The second electrode is preferably a counter electrode which performs the counterpart electrochemical reaction with oxygen. The gas sensor may include further electrodes, such as a reference electrode and/or a gas generating electrode.

The conductive mass preferably includes polymer electrolyte. The conductive mass may be a plug, pin, or other shaped component suitable for forming an electrical path between the electrodes and the external connection means.

The external connection means is preferably a porous planar element which may be formed on the substrate in an identical manner to the formation of the electrodes. Alternatively, the external connection means may be formed from the same, or a similar material, to the conductive mass. The external connection means may also be a metal strip, or wire, which is attached to the substrate.

The substrate is preferably porous, allowing gas access to the sensing electrode through the substrate, but is preferably impervious to liquid electrolyte at atmospheric pressure. The substrate material preferably allows melted polymer electrolyte to pass through it under pressure.

Preferably a wicking means is provided, the wicking means being arranged so that it is able to contact both the electrolyte and the electrodes, thereby wetting the electrodes with electrolyte.

The sensor may have a cap so that the substrate is disposed between the cap and the housing. In this particular arrangement, the substrate is preferably highly gas permeable and presents no barrier to diffusion of gas through it. In this case, diffusion of gas to the sensing electrode is preferably limited by a diffusion barrier located in the cap.

Alternatively, the sensor may have no cap, so that the substrate itself is a diffusion barrier and forms the upper part of the housing. In this case, the porosity of the substrate in certain regions is preferably decreased in order to limit the amount of

gas reaching the sensing electrode and/or the counter electrode. The substrate may be flexible, semi-rigid, or rigid.

Preferably the electrolyte is sulphuric acid or other suitable electrolyte.

A number of embodiments of the invention will now be described, by way of example only, with reference to the accompanying Figures, in which:-

Figure 1 shows a cross-section of a first gas sensor; and

Figure 2 shows a cross-section of a second gas sensor.

Referring to Figure 1 there is shown a sectional view of an electrochemical gas sensor (10a) in the form of a right circular cylinder, the sensor comprising a two part housing (12a) and (12b), a sensing electrode (14), a counter electrode (16), and external contact tracks (28a) and (28b) formed on a generally circular membrane (18). Electrodes (14) and (16) are formed from a mixture of electrically conductive catalyst particles in PTFE binder, and are screen printed or filter deposited onto the lower surface of the membrane (18) in the form of segments, as shown in the Figure. External contacts (28a) and (28b) are formed in the same way as the electrodes, but with conductive non-catalytic particles and PTFE, and are formed on the upper surface of the membrane (18).

Housing portion (12b) is cylindrical with a hollow interior defining an electrolyte reservoir (20) containing liquid electrolyte (30). Electrolyte (30) is maintained in contact with the electrodes (14,16) by means of a wick (21). The electrolyte reservoir (20) is closed at the base by means of a base member (32) having a pressure relief vent closed by a porous membrane. Housing part (12a) is a disc shaped cap member having an aperture (22) therein to permit atmospheric gas to diffuse to a recessed manifold area (24), and then to sensing electrode (14). The housing portions are composed of a synthetic plastics material. Aperture (22) may

be in the form of a diffusion barrier to control the amount of gas reaching the sensing electrode.

Membrane (18) is disc shaped and is of approximately the same diameter as lower housing portion (12b). The membrane is disposed between upper housing portion (12a) and lower housing portion (12b). As the upper housing portion (12a) is smaller in diameter than lower housing portion (12b), external contact tracks (28a) and (28b) extend past the edge of upper housing portion (12a), and may thus be used as an external electrical connection. The external electrical connection contacts may be connected to a printed circuit board and a power supply by way of pins, spring clips, or wires (not shown).

Referring now to Figure 2 which shows a sectional view of the second embodiment (10b) of the invention, similar parts to those of Figure 1 are denoted by the same reference numeral. In this embodiment of the invention, the upper cap member (12a) is not present. The membrane (18) is of a low permeability to gases in order to define a diffusion barrier for incoming gas. Thus precise control over the rate of ingress of gas is provided. The permeability of the membrane (18) may be uniform over the entire membrane, or the permeability may be reduced in a particular region by, for example, pressing or impregnating certain areas of the membrane with a suitable substrate.

In gas sensor (10b), regions of the electrodes (14) and (16) and the membrane (18) are impregnated with solid polymer electrolyte such that the SPE protrudes through the membrane (18) to form external contacts (28a) and (28b). Further external electrical contact means may then be provided, held in place by the solidified conducting polymer (26).

One advantage of the gas sensors (10a) and (10b) over existing gas sensors is that the electrodes of sensors (10a,b) do not extend into the regions between the housing and the membrane (18), which are generally the weakest part of the gas sensor assembly. Thus in gas sensors (10a) and (10b), a strong seal is formed between the housing and the membrane, and electrolyte is less likely to leak from the sensor.

During operation of gas sensors (10a) and (10b), gas from the environment diffuses through the membrane (18) (via aperture (22) for sensor (10a)) to sensing electrode (14). If this gas contains, for example, carbon monoxide, an electrochemical reaction occurs at sensing electrode (14), and an electrochemical reaction with oxygen occurs at counter electrode (16). Current is thus carried through the electrolyte (30) by ions produced in these reactions. The size of the current indicates the concentration of carbon monoxide.

A reference electrode (not shown) may be employed in combination with a potentiostat circuit to maintain the potential between the sensing electrode (14) and the electrolyte (30) in order to increase the stability of the sensor (10a).

The assembly of sensor (10a) will now be described. Electrodes (14) and (16) are formed on the lower surface of membrane (18). External contact tracks (28a) and (28b) are formed on the upper surface of this membrane. The wick (21) is then sintered to the electrodes (14) and (16). Molten polymer electrolyte (26) is introduced into required areas of the membrane (18) via holes in the wick (21), or from the upper surface of external contract tracks (28a,b), by applying heat and pressure to force the material through the membrane so a contact is made between external contacts (28a) and (28b) and electrodes (14) and (16). On solidification of the polymer electrolyte, an electrical path is formed between the electrolyte (30) contained with electrolyte reservoir (20) and the external contact tracks (28a) and (28b).

The membrane is then positioned between upper (12a) and lower housing portions (12b), and heat and pressure are applied using a press tool in order to compress the membrane and the external contacts onto the housing portions, thereby bonding the assembly together. Alternatively, one or both of the housing portions (12a,b) may be bonded to the membrane (18) using adhesive.

Electrolyte is then introduced into the electrolyte reservoir (20) via aperture (32). This aperture is then plugged with an acid-tight plug (which may be gas

permeable), and sealed in place using ultrasonic bonding. This ensures that electrolyte (30) does not leak from the sensor cell (10a).

The assembly of sensor (10b) is similar to that of sensor (10a). Electrodes (14) and (16) are formed on the lower surface of the membrane (18). If required, the permeability to gas of regions of the membrane may be decreased, as described previously. The wick (21) is then sintered to the electrodes (14) and (16). Molten polymer electrolyte (26) is introduced into required areas of the membrane (18) via holes in the wick (21), or from the upper surface of the membrane (18), by applying heat and pressure to force the material through the membrane so that, on solidification, it protrudes through the membrane (18) to form external contacts (28a) and (28b). Further external contact means may be provided, held in place by the solidified conducting polymer.

The membrane is then positioned above lower housing portion (12b), and heat and pressure are applied using a press tool in order to compress the membrane onto the housing portion, thereby bonding the assembly together. Alternatively, the lower housing portion (12b) may be bonded to the membrane (18) using adhesive. Electrolyte is then introduced into the electrolyte reservoir (20) as previously described.

Variation may be made to the aforementioned embodiments without departing from the scope of the invention. For example, for the sensors described herein, three or more electrodes may be formed on the membrane. These additional electrodes may generate a test gas so that the sensors have self-test capability.

Claims

1. A method of manufacturing a gas sensor (10) comprising the steps of: 1) forming at least and first (14) and second (16) electrodes on a planar substrate (18); 2) forming external connection means (28a,b) on the substrate; 3) introducing conductive material (26) into a portion of the substrate adjacent the external connection means (28a,b), and into the portion of electrode (14,16) adjacent said portion of substrate, so that an electrical path is formed between an electrode and the external connection means; 4) providing a housing (12a,b) containing a reservoir (20) for liquid electrolyte (30); and 5) bonding the substrate (18) and the housing (12a,b) so that a seal is formed which substantially prevents the leakage of electrolyte from the gas sensor.

2. A method according to claim 1 further including the step of attaching a wicking means (21) to the electrodes (14,16).

3. A method according to claim 2 whereby the wicking means (21) is pressed or sintered to the electrodes (14,16).

4. A method according to claim 3 whereby the wicking means (21) is sintered to the electrodes (14,16) at a temperature of between 300°C and 370°C.

5. A method according to claim 4 whereby the wicking means (21) is sintered to the electrodes (14,16) at a temperature of between 320°C and 370°C.

6. A method according to any preceding claim whereby the conductive material (26) is introduced into the substrate (18) via the wicking means (21).

7. A method according to any preceding claim whereby the conductive material (26) is introduced into the substrate (18) via an electrode (14,16).

8. A method according to any preceding claim whereby the conductive material (26) is introduced into the substrate (18) via the external connection means (28a,b).

8. A method according to any preceding claim whereby the conductive material (26) is introduced into the substrate (18) via the external connection means (28a,b).

9. A method according to any preceding claim whereby the conductive material (26) is introduced into the substrate (18) via the substrate (18).

10. A method according to any preceding claim whereby conductive material (26) in its melted state is introduced into the substrate (18).

11. A method according to any preceding claim whereby electrodes (14,16) and/or external connection means (28a,b) are formed on the substrate (18) by (a) screen printing, (b) filtering in selected areas from a suspension placed onto the substrate, (c) spray coating, or (d) sintering.

12. A method according to any preceding claim whereby the electrodes (14,16) are formed on the opposite faces of the substrate (18) to the external connection means (28a,b).

13. A method according to any of claims 1 to 8 whereby the electrodes (14,16) are formed on the same face of the substrate (18) as the external connection means (28a,b).

14. A method according to any preceding claim wherein the substrate (18) and the housing (12a,b) are bonded together using adhesive.

15. A method according to any of claims 1 to 10 wherein the substrate (18) and housing (12a,b) are bonded using heat and/or pressure so that material forming the housing melts and impregnates the substrate, thus forming a strong bond therebetween.

16. A method according to any preceding claim whereby the permeability of at least one region of the substrate (18) to gas is decreased in order to limit the amount of gas reaching an electrode.

17. A method according to claim 16 whereby the permeability of at least one region of the substrate (18) to gases is decreased by a) compressing the region, b) impregnating the region(s) with wax, c) impregnating the region(s) with a polymer, or a combination of any of steps a) to c).

18. A gas sensor (10) comprising: 1) at least first (14) and second (16) electrodes formed on a planar substrate (18); 2) a housing (12b) containing a reservoir (20) which, in use, contains liquid electrolyte (30) for contacting the first and second electrodes; 3) external connection means (28a,b), in contact with the substrate, for making external electrical connection to the gas sensor; and 4) a conductive mass (26) disposed between an electrode (14,16) and the external connection means (28a,b), wherein at least a portion of the electrode and the portion of substrate substantially adjacent thereto is impregnated by the conductive mass, the conductive mass forming an electrical path between the electrodes and the external connection means.

19. A gas sensor according to claim 18 wherein the electrodes (14,16) and/or external connection means (28a,b) are formed from a porous electrically conductive material containing catalyst material.

20. A gas sensor according to claims 18 and 19 wherein the first electrode (14) is a sensing electrode for creating the desired electrochemical reaction between the electrolyte (30) and the gas to be sensed.

21. A gas sensor according to any of claims 18 to 20 wherein the second electrode (16) is a counter electrode which performs an electrochemical reaction with oxygen.

22. A gas sensor according to any of claims 18 to 21 further including a reference electrode.

23. A gas sensor according to any of claims 18 to 22 further including a gas generating electrode.

24. A gas sensor according to any of claims 18 to 23 wherein the conductive mass (26) includes polymer electrolyte.

25. A gas sensor according to claim 24 wherein the conductive mass (26) is a plug, pin, or other shaped component suitable for forming an electrical path between the electrodes (14,16) and the external connection means (28a,b).

26. A gas sensor according to any of claims 18 to 25 wherein the external connection means (28a,b) includes polymer electrolyte.

27. A gas sensor according to any of claims 18 to 25 wherein the external connection means (28a,b) is a metal strip, or wire, which is attached to the substrate (18).

28. A gas sensor according to any of claims 18 to 27 further including a wicking means (21), the wicking means being arranged so that, in use, it contacts both the electrolyte (30) and the electrodes (14,16), thereby wetting the electrodes with electrolyte.

29. A gas sensor according to any of claims 18 to 28 wherein the wicking means (21) has at least one aperture formed therein through which polymer electrolyte (26) can be introduced.

30. A gas sensor substantially as described herein with reference to the accompanying drawing.

10a

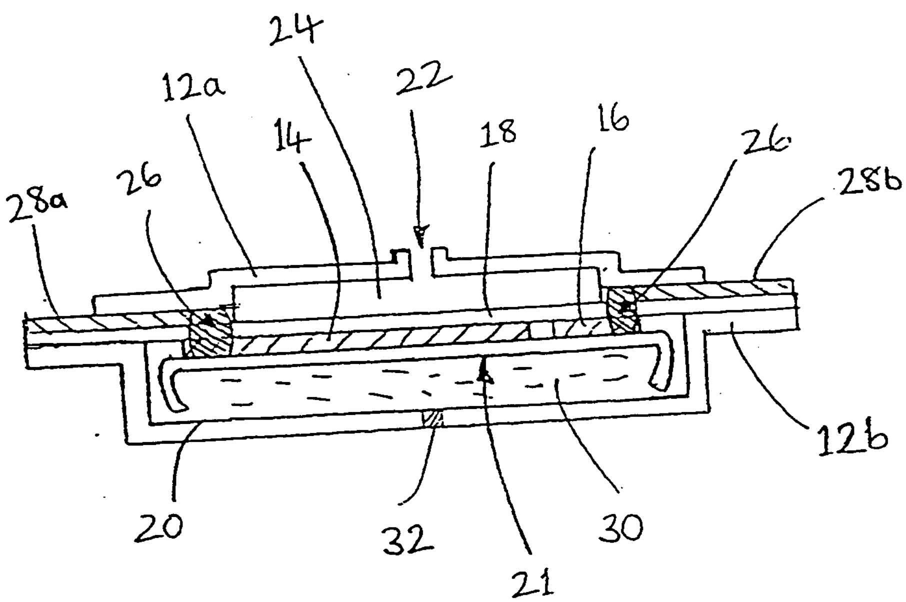

Figure 1

10b

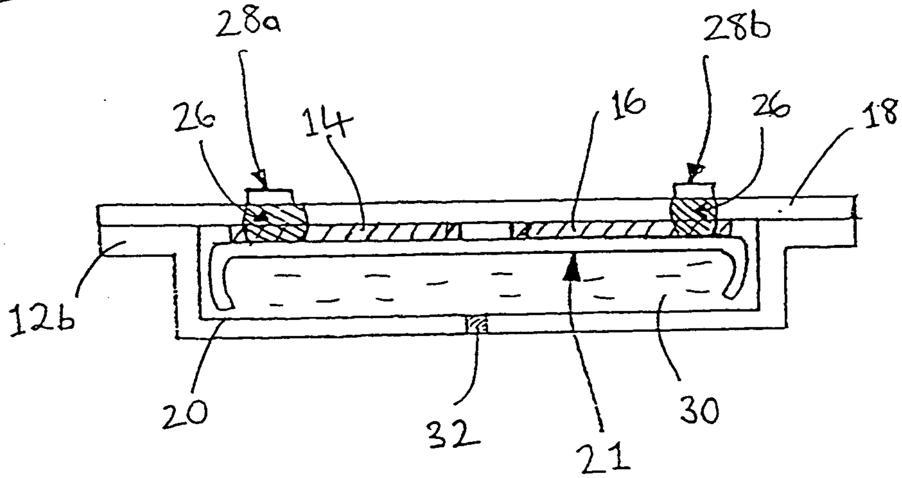

Figure 2

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